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 TI Cu-Cr-Zr alloy having excellent fatigue  
 property, its production method and cooling roll for continuous casting  
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AB The title Cu-Cr-Zr alloy contains Cr  
 0.3-0.8, Zr 0.1-0.15, Fe  $\leq$ 0.04, Ti  $\leq$ 0.02% and  
 balance Cu, wherein maximum diameter of cluster comprising  
 single or multiple Zr inclusions is  $\leq$ 15  $\mu$ m. The  
 Cu-Cr-Zr alloy is manufactured by alloying  
 Cu and Zr, pulverizing the Cu-Zr  
 alloy, and adding it to Cu alloy during its melting. Cooling  
 rolls made from the Cu-Cr-Zr alloy have  
 excellent fatigue property and service life in continuous casting.

## PATENT ABSTRACTS OF JAPAN

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(21)Application number : 2000-188375

(71)Applicant : NIPPON STEEL CORP

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(54) Cu-Cr-Zr ALLOY EXCELLENT IN FATIGUE CHARACTERISTIC, ITS PRODUCTION METHOD AND COOLING ROLL FOR CONTINUOUS CASTING

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a Cu-Cr-Zr alloy having excellent high temperature strength, thermal conductivity and fatigue resistance, to provide its production method and to provide a cooling roll for continuous casting excellent in a service life and used for continuous casting of a twin roll system or the like in which a local heat cycle load for a short time compared with a conventional system is applied.

SOLUTION: This Cu-Cr-Zr alloy excellent in fatigue characteristics has a composition containing, by mass, 0.3 to 0.8% Cr, 0.10 to 0.15% Zr,  $\leq 0.04\%$  Fe and  $\leq 0.02\%$  Ti, and the balance Cu with inevitable impurities, and in which the maximum diameter of clusters composed of single Zr-based inclusions or plural Zr-based inclusions is  $\leq 15 \mu\text{m}$ .

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CLAIMS

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[Claim(s)]

[Claim 1] At mass % , they are Cr:0.3% - 0.8%, Zr:0.10% -0.15%, and Fe:0.04%. The following and Ti:0.02% The overall diameter of a cluster which the following is contained, and the remainder consists of Cu and an unescapable impurity, and consists of independent Zr system inclusion or two or more Zr system inclusion is 15 micrometers. Cu-Cr-Zr system alloy excellent in the fatigue property characterized by consisting of the following.

[Claim 2] By mass % , Cr:0.3% - 0.8% and Zr:0.10% -0.15%, Fe: 0.04% The following and Ti:0.02% Contain the following and the remainder consists of Cu and an unescapable impurity. The Cu-Cr-Zr system alloy excellent in the fatigue property that the cluster which an overall diameter becomes from 15-micrometer or more independent Zr system inclusion or two or more Zr system inclusion 50 micrometers or less is characterized by consisting or less [ per piece/mm ] of two.

[Claim 3] The manufacture approach of a Cu-Cr-Zr system alloy excellent in the fatigue property characterized by facing manufacturing a Cu-Cr-Zr system alloy according to claim 1 or 2, grinding as the Zr addition approach at the time of the dissolution after alloying Cu-Zr beforehand, and adding at the time of the dissolution.

[Claim 4] The cooling roller for continuous casting characterized by a less than 50mm field consisting of a Cu-Cr-Zr system alloy according to claim 1 or 2 from the maximum front face in the thickness direction.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the structure of the cooling roller further used for the continuous casting by the congruence roll method using the alloy, the single roll method, or the block method about the Cu-Cr-Zr system alloy of which the high intensity in an elevated temperature, high temperature conductivity, and a fatigue-proof property are required, and its manufacture approach.

[0002]

[Description of the Prior Art] Generally, high temperature strength, the high temperature conductivity of the property for which the mold for casting is asked, etc. are cores. Then, precipitation-hardening mold Cu alloys, such as a Cu-Be system alloy, have been used until now. Especially, since the Cu-Cr-Zr system alloy is excellent in high temperature strength and the balance of high temperature conductivity, various examination, such as the component system, manufacture conditions, etc., has been made. For example, patent 2863627th In the number official report, the mold material for continuous casting which is excellent in high temperature strength by specifying the combination of solution treatment, heat treatment which follows it, and processing conditions is proposed. Moreover, in JP,07-11363,A, in order to obtain the copper alloy member which is excellent in high intensity and quantity conductivity, a kind was chosen from Cr, Zr, and Ti at least, and the manufacture approach characterized by performing aging treatment further in two steps etc. is proposed as the copper alloy member which specified the rate of the amount of alloying elements, and the amount of dissolution. Furthermore, in JP,9-87815,A, it has proposed specifying a grain size number below as 0.075 mm by specifying manufacture conditions as a chromium zirconium system copper alloy material used for the mold of the continuous casting which is excellent in a thermal fatigue property.

[0003] When casting according [ a place ] for example, to a congruence roll method etc. came to be considered, compared with the conventional mold, it was a short time remarkably, and since a local heat cycle load was moreover received, the use life expected not necessarily was not able to be shown in the cooling roller used for such casting only by satisfying the above-mentioned property. So, in JP,7-113133,B, the copper alloy excellent in reinforcement, thermal conductivity, and abrasion resistance is proposed by specifying the content of Li added to a Cr-Zr alloy as the usual continuous casting mold or a cooling roller for amorphous alloy thin object manufacture, or aluminum. However, in a Prior art, the direct factor exerted on a fatigue property was not clarified, and sufficient cure was not solved.

[0004] That is, supply of the Cu-Cr-Zr system alloy which was excellent in heat-resistant fatigue more than before came to be desired by examining the factor exerted on a fatigue property.

[0005]

[Problem(s) to be Solved by the Invention] Then, while having the high temperature strength and the high temperature conductivity which be excellent in this invention from the above-mentioned viewpoint, compared with the Cu-Cr-Zr system alloy excellent in the fatigue-proof property, and the manufacture approach and the further conventional mold, it be a short time remarkably, and aim at offering the cooling roller for continuous casting excellent in the use life use for continuous casting, such as a congruence roll method which moreover receive a local heat cycle load.

[0006]

[Means for Solving the Problem] this invention persons acquired the following knowledge, as a result of studying the factor exerted on high temperature strength and the fatigue property of a Cu-Cr-Zr system alloy of having high temperature conductivity. That is, by the conventional manufacture approach, in a solubilization -

solution treatment process, in order to prevent an alloying element wearing down by oxidation etc., the above alloying element originally needed is added. However, if a high-melting precipitation-hardening mold element is added superfluously, even if it can solidify before being able to make it dissolve completely, or it can dissolve, a suitable cooling rate will not be obtained depending on the size of casting, but crystallization and growth of a crystal will take place in a coagulation process. Then, an overall diameter is 15 micrometers as a result of investigating the relation between various non-melts, a crystallization object, and a fatigue property. Zr simple substance which is not dissolved [ of a more than ], It is the intermetallic compound ( $Cu_xZr$  system intermetallic compounds, such as Zr simple substance and  $Cu_3Zr$ , are called Zr system inclusion below) of  $Cu_3Zr$  to a  $Cr_xZr$  system intermetallic compound and the Lord. Near tends to serve as an origin of fatigue breaking. It found out that manufactures, such as a cooling roller, produced fatigue breaking easily by the heat cycle, and served as a short life as a result.

[0007] The place made into the summary of this invention is (1) mass % . Namely, Cr:0.3% - 0.8%, Zr: 0.10% - 0.15% and Fe:0.04% The following and Ti:0.02% The following is contained. For the remainder, the overall diameter of two or more Zr system inclusion which consists of Cu and an unescapable impurity and forms independent Zr system inclusion or a cluster is 15 micrometers. The Cu-Cr-Zr system alloy excellent in the fatigue property characterized by consisting of the following, (2) By mass % , Cr:0.3% - 0.8% and Zr:0.10% - 0.15%, Fe: 0.04% The following and Ti:0.02% Contain the following and the remainder consists of Cu and an unescapable impurity. The cluster which an overall diameter becomes from independent Zr system inclusion or two or more Zr system inclusion 50 micrometers or less by 15 micrometers or more 1 piece/mm<sup>2</sup> It faces manufacturing a Cu-Cr-Zr system alloy the Cu-Cr-Zr system alloy excellent in the fatigue property characterized by being the following, (3) above (1), or given in (2). As the Zr addition approach at the time of the dissolution The manufacture approach of a Cu-Cr-Zr system alloy excellent in the fatigue property characterized by grinding after alloying Cu-Zr beforehand, and adding at the time of the dissolution, (4) It is in the cooling roller for continuous casting characterized by a less than 50mm field consisting of a Cu-Cr-Zr system alloy the above (1) or given in (2) from the maximum front face in the thickness direction.

[0008]

[Embodiment of the Invention] In this invention, the reason for having specified the component presentation range, and the class and size of inclusion is as follows.

(a) The component presentation Cr is 0.3% (it is the same mass % and the following), although there is an operation which carries out a detailed deposit by solution treatment - aging treatment, and raises high temperature strength. In the following, even if the effectiveness is not acquired enough but exceeds 0.8% on the other hand, the improvement with the remarkable effectiveness is not found.

[0009] Zr has the operation which improves the reinforcement in an elevated temperature, and ductility while it similarly deposits as detailed  $Cu_3Zr$  by solution treatment - aging treatment and carries out grain refining of the crystal grain. However, at less than 0.1%, the effectiveness of precipitation hardening is not acquired enough, but it is 0.15%. If it exceeds, it cannot be made to dissolve completely also at solution treatment temperature, but un-dissolving [ the amount of ] will remain, and it will become the cause of reducing a fatigue property.

[0010] Fe is 0.04% in order to secure the thermal conductivity which was excellent in order to make conductivity low. It is necessary to specify below. Ti is 0.02% in order to secure the thermal conductivity which was similarly excellent in order to make conductivity low like Fe. It is necessary to specify below. In addition, in this invention, even if it contains As, Co, P, Sb, and Ir and contains Ag, aluminum, Mg, nickel, Be, Pb, and Zn for germanium, Mn, Si, Sn, and In other than the above-mentioned component 0.001 to 0.50% or less 0.001 to 0.10% or less 0.001 to 0.04% or less, respectively, it is possible to acquire the effectiveness of this invention.

(b) The inclusion of the class and size Cr system of inclusion is comparatively rich in ductility, and since it is rare to produce mismatching with a base at the time of processing by forging, rolling, etc., the marked consideration to a fatigue property is not accepted.

[0011] On the other hand, the inclusion of Zr system is lacking in ductility, and especially the inclusion for un-dissolving hardly shows adjustment with a base, but when remarkable, it is forging or a strip-processing process, and exfoliation with a base is seen. In order to acquire the outstanding fatigue-proof property from such a viewpoint, it is necessary to control the cluster which consists of Zr system inclusion or such inclusion. Then, the cluster which consists of Zr system inclusion exceeding 15 micrometers or two or more Zr system inclusion is 15 micrometers about the overall diameter of a cluster which consists of independent Zr system inclusion or two or more Zr system inclusion in order to reduce a fatigue property remarkably. It was determined as the

following. Moreover, 15 micrometers The size is 50 micrometers even if the above inclusion exists. Below, it is 2 1mm. The cluster which an overall diameter becomes from independent Zr system inclusion or two or more Zr system inclusion 50 micrometers or less by 15 micrometers or more since it is economically effective in within the limits, if it is one or less piece is 2 one piece/mm. It also made to be the following into the convention range.

[0012] The above-mentioned inclusion and observation of a cluster grind the part of arbitration mechanically, the size and distribution condition are observed by SEM (scanning electron microscope), and they observe one inclusion [ one ] or the cluster in the location of at least ten or more visual fields by 500 or more times desirably 300 or more times, and maximum length of cross-section die length is made into the overall diameter, and it can carry out by identifying Zr system inclusion by SEM-EDX (energy dispersion X-ray analysis). Moreover, in the case of a cluster, spacing of inclusion makes an ensemble 5 micrometers or less the same cluster, and the maximum length of the cluster is defined as an overall diameter.

(c) Although it is possible to lengthen solution treatment time amount or to make quick cooling rates, such as the compulsory circulating water cold, as an approach of controlling the overall diameter of addition approach Zr system inclusion to convention within the limits of this invention, the manufacture time necessary for completion becomes long, or the facility correspondence for performing uniform cooling becomes disadvantageous economically. Then, the method of making an alloying element dissolve certainly at the time of the dissolution and coagulation is desirable. However, by the approach of adding Zr independently, since Zr is a refractory metal and it is easy to oxidize, in order to make it dissolve completely, it becomes difficult [ spending long time amount ] to make a component guess right. Then, uniform and high addition of hitting ratio can be performed by manufacturing and pulverizing a Cu-Zr alloy beforehand and adding at the time of the dissolution. Especially the particle size of the Cu-Zr alloy after pulverizing is 5.6mm or less (JIS Z 8801 : the sifting-out method according to a sieve the nominal dimension of 5.6mm etc.), in order to avoid the imperfect dissolution, although the effectiveness of this invention can be acquired without setting. Carrying out is desirable.

(d) Even if it is going to make the cooling rate after solution treatment quick according to a convention of the structure above-mentioned, generally the structures, such as mold, have thick thickness and cannot obtain sufficient cooling rate from the heat capacity and high temperature conductivity in many cases. However, since mold which is used for continuous casting is cooled from a inner layer, the range of which a fatigue property is required is restricted to a surface part. Then, the cooling roller which was excellent in the high intensity in an elevated temperature, high temperature conductivity, and a fatigue-proof property also in the large continuous casting of heat cycle loads, such as a cooling roller for continuous casting characterized by a field 50mm or less consisting of a Cu-Cr-Zr system alloy the above (1) or given in (2), then a congruence roll method, from the maximum front face in the thickness direction can be obtained.

[0013] In the field in which a Cu-Cr-Zr system alloy the above (1) or given in (2) exceeds 50mm in the thickness direction from the maximum front face of a cooling roller, since the effect of a thermal strain does not become large by cooling of the cooling water which flows a inner layer, it limits to the above-mentioned range. Although parts other than the surface of a cooling roller can also be made into the quality of the material beyond the convention range of this invention , when it be difficult to realize by integral construction , it be desirable that consider as the double layer structure divided into the surface section and the inner layer section , manufacture with the alloy of the same component system in order to ease distortion by the thermal stress further generated in the interface of a inner layer and a surface , and only a surface perform size control of Zr system inclusion or a cluster .

[0014] Although it burns as an approach of combining a surface and a inner layer, it inserts in and law, the pasting-up method, etc. can be considered, it does not specify especially.

[0015]

[Example] [Example 1] This invention is concretely explained based on an example below. First, oxygen free copper, the alloying element (Cr, Zr), and Cu alloy that consists of an unescapable impurity were completely dissolved at 1200 degrees C so that it might become the component indicated to Table 1 with the usual induction heating furnace, and it cast to water-cooled mold, and the 30kg ingot was ingoted. Zr added except for some test coupons on that occasion manufactured the Zr-Cu alloy 50% beforehand, pulverized it to 5.6 or less mm, and was supplied at the time of the dissolution (alloy addition).

[0016]

[Table 1]

No	C r (wt%)	Z r (wt%)	F e (wt%)	T i (wt%)	C u + 不純物	Z r 添加方法	備考
1	0.80	0.15	0.01	0.00	残	合金添加	本発明例
2	0.79	0.12	0.01	0.01	残	合金添加	本発明例
3	0.41	0.15	0.01	0.00	残	合金添加	本発明例
4	0.40	0.11	0.02	0.00	残	合金添加	本発明例
5	0.72	0.15	0.01	0.01	残	単独添加	本発明例
6	1.05	0.30	0.03	0.02	残	合金添加	比較例
7	0.29	0.05	0.01	0.01	残	合金添加	比較例
8	0.89	0.26	0.02	0.00	残	合金添加	比較例
9	0.78	0.15	0.02	0.01	残	単独添加	比較例
10	0.80	0.15	0.05	0.03	残	合金添加	比較例

After casting, after carrying out grinding of the front face, it heated at the temperature of 900 \*\* for 1 hour, and forged between heat, and it considered as the tabular sample with a thickness 45 mm x width of face of 75mm. It heated at the temperature of 975 \*\* succeedingly for 1 hour, and quenched underwater (solution treatment). Furthermore, it is 30% at ordinary temperature. After forging, heat treatment of 2 hours was performed at the temperature of 475 \*\* (aging treatment).

[0017] The mechanical property in an elevated temperature and thermal conductivity property of the example of this invention acquired on this manufacture condition and the example of a comparison, the property of inclusion, and the fatigue property were investigated. The mechanical property evaluated the tensile test in 300 \*\*, and the heat-conduction property by measuring conductivity, 20 visual fields (a cluster is included) of inclusion were observed by one 500 times the scale factor of this by SEM (scanning electron microscope), and it evaluated the component system for the size (overall diameter) and distribution condition by EDX (energy dispersion X-ray analysis). Furthermore, a fatigue property is 2 \*\*23 kgf/mm. A repeat \*\*\*\* compression fatigue test is performed at 300 degrees C, and a load is 10%. The time of falling above was judged to be destruction. The target in that case is 2x105. It carried out to more than the time. They are Table 2 and Table 3 about these results. It is shown.

[0018]

[Table 2]



No.	最大介在物サイズ ( $\mu\text{m}$ )	15~50 $\mu\text{m}$ 介在物密度 (個/ $\text{mm}^2$ )	備 考
1	14	0	本発明例
2	10	0	本発明例
3	15	0	本発明例
4	12	0	本発明例
5	15	1	本発明例
6	125	3	比較例
7	6	0	比較例
8	51	3	比較例
9	102	8	比較例
10	13	1	比較例

[0019]

[Table 3]

No.	機械的性質(300℃)			導電率 (% IACS)	破断までの 繰返し数 ( $10^5$ 回)	備考
	0.2%耐力 ( $\text{kgf}/\text{mm}^2$ )	引張強さ ( $\text{kgf}/\text{mm}^2$ )	伸び (%)			
1	38.5	40.0	10.5	85	5.1	本発明例
2	38.8	40.6	10.1	83	4.6	本発明例
3	36.8	37.8	11.6	88	2.8	本発明例
4	38.3	39.6	9.6	88	3.4	本発明例
5	37.9	39.8	10.6	85	2.1	本発明例
6	38.7	39.9	14.1	78	0.9	比較例
7	32.2	34.4	3.9	91	0.8	比較例
8	38.2	40.5	13.3	80	1.2	比較例
9	39.6	40.7	10.2	84	0.6	比較例
10	37.9	39.6	10.5	73	4.7	比較例

No.1-5 It is within the limits which also specifies the overall diameter of Zr system inclusion, and a consistency by this invention by within the limits [ an alloy content specifies each by this invention ]. In these cases, it is all the mechanical property and heat-conduction property (conductivity) in an elevated temperature. The good property was shown. On the other hand, No.6-8 The alloy content of Cr and Zr has separated from the range specified by this invention. In this case, the mechanical property and thermal conductivity (conductivity) in an elevated temperature Although inferiority is not seen to the example of this invention, the number of repeats to

fracture does not reach a target, but the fatigue property is inferior. this cause -- Table 2 or [ that Zr system inclusion is large compared with the example of this invention so that it may be shown ] -- or it is because many. Moreover, although the alloy content of No.9 was convention within the limits of this invention, since Zr was added independently, it did not result in the full dissolution but the overall diameter and consistency of inclusion separated from the convention range of this invention. Consequently, the number of repeats to fracture cannot reach a target, but the fatigue property is inferior. No.10 Although \*\* and inclusion are convention within the limits and the fatigue property is also excellent, since Fe and Ti component have separated from the convention range, conductivity has separated from the target (thermal conductivity is inferior).

[Example 2] In order to evaluate the effectiveness of casting size, they are the thickness of 300mm, and 400kg about the alloy of No.1 of Table 1. It cast to the ingot. Casting manufacture conditions, and subsequent processings - heat treatment conditions were made into an example 1 and these conditions (No.11: example of a comparison).

[0020] The property of the example of this invention of No.11 and No.1 acquired on this manufacture condition is compared, and it is shown in Table 4. Compared with the example of this invention, the amount of Zr system inclusion in which the cluster was formed increased the example of a comparison, and, as a result, the fatigue property fell remarkably.

[0021]

[Table 4]

	最大介在物サイズ ( $\mu\text{m}$ )	15~50 $\mu\text{m}$ 介在物密度 (個/ $\text{mm}^2$ )	機械的性質(300℃)			導伝率 (% IACS)	破断までの 繰り返し数 ( $10^5$ 回)	備考
			$\sigma_{0.2}$ ( $\text{kgf}/\text{mm}^2$ )	TS ( $\text{kgf}/\text{mm}^2$ )	EL (%)			
No 1	14	0	38.5	40.0	10.5	85	5.1	本発明例
No 11	97	5	36.7	37.8	10.0	86	1.9	比較例

The result shown in Table 3 and Table 4 shows that the good property of the balance which the examples of this invention are not only high temperature strength and high temperature transmissibility, but was excellent in the fatigue-proof property compared with the example of a comparison is shown.

[Example 3] In manufacturing the cooling roller for casting of the outer diameter of 900mm, the bore of 600mm, and 1000mm of drum length, 5.5t of alloys of table 1No.1 was cast, and hot forging, solution treatment, and cold forging were performed. The manufacture conditions in that case were made into an example 1 and these conditions (No.12: example of a comparison). On the other hand, similarly 2t of alloys of table 1No.1 was cast to the cooling roller for two-layer structure surfaces with an outer diameter [ of 900mm ], and a bore of 800mm, and hot forging, solution treatment, and cold forging were performed to it. The manufacture conditions in that case were also made into an example 1 and these conditions (No.13: example of this invention).

[0022] In addition, after casting and carrying out hot forging of the alloy of table 1No.1 the same also as a roll

for inner layers of the example of this invention and carrying out machining of the front face, it burned with the cooling roller for surfaces, and inserted in, and it combined by law. Example of a comparison acquired on this manufacture condition (No.12) Example of this invention (No.13) A surface property is compared and it is shown in Table 5. Compared with the example of this invention, the amount of Zr system inclusion in which the cluster was formed increased the example of a comparison, and, as a result, the fatigue property fell remarkably.

[0023]

[Table 5]

	最大介在物サイズ ( $\mu\text{m}$ )	15~50 $\mu\text{m}$ 介在物密度 (個/ $\text{mm}^2$ )	機械的性質(300°C)			導伝率 (% IACS)	破断までの繰り返し数 ( $10^5$ 回)	備考
			$\sigma_{0.2}$ ( $\text{kgf}/\text{mm}^2$ )	TS ( $\text{kgf}/\text{mm}^2$ )	El (%)			
No.12	215	13	35.8	38.1	9.8	82	0.9	比較例
No.13	14	0	38.5	40.0	10.5	85	5.1	本発明例

[0024]

[Effect of the Invention] If the Cu-Cr-Zr alloy by this invention is used for the cooling roller for continuous casting by the member of which a heat-resistant prolonged fatigue property is required especially, for example, the congruence rolling method, as stated above, it will become usable over a long period of time, and

remarkable effectiveness will be acquired economically.

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TECHNICAL FIELD

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PRIOR ART

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[Description of the Prior Art] Generally, high temperature strength, the high temperature conductivity of the property for which the mold for casting is asked, etc. are cores. Then, precipitation-hardening mold Cu alloys, such as a Cu-Be system alloy, have been used until now. Especially, since the Cu-Cr-Zr system alloy is excellent in high temperature strength and the balance of high temperature conductivity, various examination, such as the component system, manufacture conditions, etc., has been made. For example, patent 2863627th In the number official report, the mold material for continuous casting which is excellent in high temperature strength by specifying the combination of solution treatment, heat treatment which follows it, and processing conditions is proposed. Moreover, in JP,07-11363,A, in order to obtain the copper alloy member which is excellent in high intensity and quantity conductivity, a kind was chosen from Cr, Zr, and Ti at least, and the manufacture approach characterized by performing aging treatment further in two steps etc. is proposed as the copper alloy member which specified the rate of the amount of alloying elements, and the amount of dissolution. Furthermore, in JP,9-87815,A, it has proposed specifying a grain size number below as 0.075 mm by specifying manufacture conditions as a chromium zirconium system copper alloy material used for the mold of the continuous casting which is excellent in a thermal fatigue property.

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EFFECT OF THE INVENTION

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[Effect of the Invention] If the Cu-Cr-Zr alloy by this invention is used for the cooling roller for continuous casting by the member of which a heat-resistant prolonged fatigue property is required especially, for example, the congruence rolling method, as stated above, it will become usable over a long period of time, and remarkable effectiveness will be acquired economically.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] Then, while having the high temperature strength and the high temperature conductivity which be excellent in this invention from the above-mentioned viewpoint, compared with the Cu-Cr-Zr system alloy excellent in the fatigue-proof property, and the manufacture approach and the further conventional mold, it be a short time remarkably, and aim at offering the cooling roller for continuous casting excellent in the use life use for continuous casting, such as a congruence roll method which moreover receive a local heat cycle load.

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MEANS

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[Means for Solving the Problem] this invention persons acquired the following knowledge, as a result of studying the factor exerted on high temperature strength and the fatigue property of a Cu-Cr-Zr system alloy of having high temperature conductivity. That is, by the conventional manufacture approach, in a solubilization - solution treatment process, in order to prevent an alloying element wearing down by oxidation etc., the above alloying element originally needed is added. However, if a high-melting precipitation-hardening mold element is added superfluously, even if it can solidify before being able to make it dissolve completely, or it can dissolve, a suitable cooling rate will not be obtained depending on the size of casting, but crystallization and growth of a crystal will take place in a coagulation process. Then, an overall diameter is 15 micrometers as a result of investigating the relation between various non-melts, a crystallization object, and a fatigue property. Zr simple substance which is not dissolved [ of a more than ], It is the intermetallic compound (Cu<sub>x</sub> Zr system intermetallic compounds, such as Zr simple substance and Cu<sub>3</sub> Zr, are called Zr system inclusion below) of Cu<sub>3</sub> Zr to a Cr<sub>x</sub> Zr system intermetallic compound and the Lord. Near tends to serve as an origin of fatigue breaking. It found out that manufactures, such as a cooling roller, produced fatigue breaking easily by the heat cycle, and served as a short life as a result.

[0007] The place made into the summary of this invention is (1) mass % . Namely, Cr:0.3% - 0.8%, Zr: 0.10% - 0.15% and Fe:0.04% The following and Ti:0.02% The following is contained. For the remainder, the overall diameter of two or more Zr system inclusion which consists of Cu and an unescapable impurity and forms independent Zr system inclusion or a cluster is 15 micrometers. The Cu-Cr-Zr system alloy excellent in the fatigue property characterized by consisting of the following, (2) By mass % , Cr:0.3% - 0.8% and Zr:0.10% - 0.15%, Fe: 0.04% The following and Ti:0.02% Contain the following and the remainder consists of Cu and an unescapable impurity. The cluster which an overall diameter becomes from independent Zr system inclusion or two or more Zr system inclusion 50 micrometers or less by 15 micrometers or more 1 piece/mm<sup>2</sup> It faces manufacturing a Cu-Cr-Zr system alloy the Cu-Cr-Zr system alloy excellent in the fatigue property characterized by being the following, (3) above (1), or given in (2). As the Zr addition approach at the time of the dissolution The manufacture approach of a Cu-Cr-Zr system alloy excellent in the fatigue property characterized by grinding after alloying Cu-Zr beforehand, and adding at the time of the dissolution, (4) It is in the cooling roller for continuous casting characterized by a less than 50mm field consisting of a Cu-Cr-Zr system alloy the above (1) or given in (2) from the maximum front face in the thickness direction.

[0008]

[Embodiment of the Invention] In this invention, the reason for having specified the component presentation range, and the class and size of inclusion is as follows.

(a) The component presentation Cr is 0.3% (it is the same mass % and the following), although there is an operation which carries out a detailed deposit by solution treatment - aging treatment, and raises high temperature strength. In the following, even if the effectiveness is not acquired enough but exceeds 0.8% on the other hand, the improvement with the remarkable effectiveness is not found.

[0009] Zr has the operation which improves the reinforcement in an elevated temperature, and ductility while it similarly deposits as detailed Cu<sub>3</sub> Zr by solution treatment - aging treatment and carries out grain refining of the crystal grain. However, at less than 0.1%, the effectiveness of precipitation hardening is not acquired enough, but it is 0.15%. If it exceeds, it cannot be made to dissolve completely also at solution treatment temperature, but un-dissolving [ the amount of ] will remain, and it will become the cause of reducing a fatigue property.

[0010] Fe is 0.04% in order to secure the thermal conductivity which was excellent in order to make conductivity low. It is necessary to specify below. Ti is 0.02% in order to secure the thermal conductivity which

was similarly excellent in order to make conductivity low like Fe. It is necessary to specify below. In addition, in this invention, even if it contains As, Co, P, Sb, and Ir and contains Ag, aluminum, Mg, nickel, Be, Pb, and Zn for germanium, Mn, Si, Sn, and In other than the above-mentioned component 0.001 to 0.50% or less 0.001 to 0.10% or less 0.001 to 0.04% or less, respectively, it is possible to acquire the effectiveness of this invention.

(b) The inclusion of the class and size Cr system of inclusion is comparatively rich in ductility, and since it is rare to produce mismatching with a base at the time of processing by forging, rolling, etc., the marked consideration to a fatigue property is not accepted.

[0011] On the other hand, the inclusion of Zr system is lacking in ductility, and especially the inclusion for undissolving hardly shows adjustment with a base, but when remarkable, it is forging or a strip-processing process, and exfoliation with a base is seen. In order to acquire the outstanding fatigue-proof property from such a viewpoint, it is necessary to control the cluster which consists of Zr system inclusion or such inclusion. Then, the cluster which consists of Zr system inclusion exceeding 15 micrometers or two or more Zr system inclusion is 15 micrometers about the overall diameter of a cluster which consists of independent Zr system inclusion or two or more Zr system inclusion in order to reduce a fatigue property remarkably. It was determined as the following. Moreover, 15 micrometers The size is 50 micrometers even if the above inclusion exists. Below, it is 2 mm. The cluster which an overall diameter becomes from independent Zr system inclusion or two or more Zr system inclusion 50 micrometers or less by 15 micrometers or more since it is economically effective in within the limits, if it is one or less piece is 2 one piece/mm. It also made to be the following into the convention range.

[0012] The above-mentioned inclusion and observation of a cluster grind the part of arbitration mechanically, the size and distribution condition are observed by SEM (scanning electron microscope), and they observe one inclusion [ one ] or the cluster in the location of at least ten or more visual fields by 500 or more times desirably 300 or more times, and maximum length of cross-section die length is made into the overall diameter, and it can carry out by identifying Zr system inclusion by SEM-EDX (energy dispersion X-ray analysis). Moreover, in the case of a cluster, spacing of inclusion makes an ensemble 5 micrometers or less the same cluster, and the maximum length of the cluster is defined as an overall diameter.

(c) Although it is possible to lengthen solution treatment time amount or to make quick cooling rates, such as the compulsory circulating water cold, as an approach of controlling the overall diameter of addition approach Zr system inclusion to convention within the limits of this invention, the manufacture time necessary for completion becomes long, or the facility correspondence for performing uniform cooling becomes disadvantageous economically. Then, the method of making an alloying element dissolve certainly at the time of the dissolution and coagulation is desirable. However, by the approach of adding Zr independently, since Zr is a refractory metal and it is easy to oxidize, in order to make it dissolve completely, it becomes difficult [ spending long time amount ] to make a component guess right. Then, uniform and high addition of hitting ratio can be performed by manufacturing and pulverizing a Cu-Zr alloy beforehand and adding at the time of the dissolution. Especially the particle size of the Cu-Zr alloy after pulverizing is 5.6mm or less (JIS Z 8801 : the sifting-out method according to a sieve the nominal dimension of 5.6mm etc.), in order to avoid the imperfect dissolution, although the effectiveness of this invention can be acquired without setting. Carrying out is desirable.

(d) Even if it is going to make the cooling rate after solution treatment quick according to a convention of the structure above-mentioned, generally the structures, such as mold, have thick thickness and cannot obtain sufficient cooling rate from the heat capacity and high temperature conductivity in many cases. However, since mold which is used for continuous casting is cooled from an inner layer, the range of which a fatigue property is required is restricted to a surface part. Then, the cooling roller which was excellent in the high intensity in an elevated temperature, high temperature conductivity, and a fatigue-proof property also in the large continuous casting of heat cycle loads, such as a cooling roller for continuous casting characterized by a field 50mm or less consisting of a Cu-Cr-Zr system alloy the above (1) or given in (2), then a congruence roll method, from the maximum front face in the thickness direction can be obtained.

[0013] In the field in which a Cu-Cr-Zr system alloy the above (1) or given in (2) exceeds 50mm in the thickness direction from the maximum front face of a cooling roller, since the effect of a thermal strain does not become large by cooling of the cooling water which flows an inner layer, it limits to the above-mentioned range. Although parts other than the surface of a cooling roller can also be made into the quality of the material beyond the convention range of this invention, when it be difficult to realize by integral construction, it be desirable

that consider as the double layer structure divided into the surface section and the inner layer section , manufacture with the alloy of the same component system in order to ease distortion by the thermal stress further generated in the interface of a inner layer and a surface , and only a surface perform size control of Zr system inclusion or a cluster .

[0014] Although it burns as an approach of combining a surface and a inner layer, it inserts in and law, the pasting-up method, etc. can be considered, it does not specify especially.

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## EXAMPLE

[Example] [Example 1] This invention is concretely explained based on an example below. First, oxygen free copper, the alloying element (Cr, Zr), and Cu alloy that consists of an unescapable impurity were completely dissolved at 1200 degrees C so that it might become the component indicated to Table 1 with the usual induction heating furnace, and it cast to water-cooled mold, and the 30kg ingot was ingoted. Zr added except for some test coupons on that occasion manufactured the Zr-Cu alloy 50% beforehand, pulverized it to 5.6 or less mm, and was supplied at the time of the dissolution (alloy addition).

[0016]

[Table 1]

No	Cr (wt%)	Zr (wt%)	Fe (wt%)	Ti (wt%)	Cu+ 不純物	Zr 添加方法	備考
1	0.80	0.15	0.01	0.00	残	合金添加	本発明例
2	0.79	0.12	0.01	0.01	残	合金添加	本発明例
3	0.41	0.15	0.01	0.00	残	合金添加	本発明例
4	0.40	0.11	0.02	0.00	残	合金添加	本発明例
5	0.72	0.15	0.01	0.01	残	単独添加	本発明例
6	1.05	0.30	0.03	0.02	残	合金添加	比較例
7	0.29	0.05	0.01	0.01	残	合金添加	比較例
8	0.89	0.26	0.02	0.00	残	合金添加	比較例
9	0.78	0.15	0.02	0.01	残	単独添加	比較例
10	0.80	0.15	0.05	0.03	残	合金添加	比較例

After casting, after carrying out grinding of the front face, it heated at the temperature of 900 \*\* for 1 hour, and forged between heat, and it considered as the tabular sample with a thickness 45 mm x width of face of 75mm. It heated at the temperature of 975 \*\* succeedingly for 1 hour, and quenched underwater (solution treatment). Furthermore, it is 30% at ordinary temperature. After forging, heat treatment of 2 hours was performed at the temperature of 475 \*\* (aging treatment).

[0017] The mechanical property in an elevated temperature and thermal conductivity property of the example of this invention acquired on this manufacture condition and the example of a comparison, the property of inclusion, and the fatigue property were investigated. The mechanical property evaluated the tensile test in 300 \*\*, and the heat-conduction property by measuring conductivity, 20 visual fields (a cluster is included) of inclusion were observed by one 500 times the scale factor of this by SEM (scanning electron microscope), and it evaluated the component system for the size (overall diameter) and distribution condition by EDX (energy dispersion X-ray analysis). Furthermore, a fatigue property is 2 \*\*23 kgf/mm. A repeat \*\*\*\* compression

fatigue test is performed at 300 degrees C, and a load is 10%. The time of falling above was judged to be destruction. The target in that case is  $2 \times 10^5$ . It carried out to more than the time. They are Table 2 and Table 3 about these results. It is shown.

[0018]

[Table 2]

No	最大介在物サイズ ( $\mu\text{m}$ )	15～50 $\mu\text{m}$ 介在物密度 (個/ $\text{mm}^2$ )	備 考
1	14	0	本発明例
2	10	0	本発明例
3	15	0	本発明例
4	12	0	本発明例
5	15	1	本発明例
6	125	3	比較例
7	6	0	比較例
8	51	3	比較例
9	102	8	比較例
10	13	1	比較例

[0019]

[Table 3]

No	機械的性質(300℃)			導電率 (% IACS)	破断までの 繰返し数 ( $10^5$ 回)	備考
	0.2%耐力 ( $\text{kgf}/\text{mm}^2$ )	引張強さ ( $\text{kgf}/\text{mm}^2$ )	伸び (%)			
1	38.5	40.0	10.5	85	5.1	本発明例
2	38.8	40.6	10.1	83	4.6	本発明例
3	36.8	37.8	11.6	88	2.8	本発明例
4	38.3	39.6	9.6	88	3.4	本発明例
5	37.9	39.8	10.6	85	2.1	本発明例
6	38.7	39.9	14.1	78	0.9	比較例
7	32.2	34.4	3.9	91	0.8	比較例
8	38.2	40.5	13.3	80	1.2	比較例
9	39.6	40.7	10.2	84	0.6	比較例
10	37.9	39.6	10.5	73	4.7	比較例

No.1-5 It is within the limits which also specifies the overall diameter of Zr system inclusion, and a consistency

by this invention by within the limits [ an alloy content specifies each by this invention ]. In these cases, it is all the mechanical property and heat-conduction property (conductivity) in an elevated temperature. The good property was shown. On the other hand, No.6-8 The alloy content of Cr and Zr has separated from the range specified by this invention. In this case, the mechanical property and thermal conductivity (conductivity) in an elevated temperature Although inferiority is not seen to the example of this invention, the number of repeats to fracture does not reach a target, but the fatigue property is inferior. this cause -- Table 2 or [ that Zr system inclusion is large compared with the example of this invention so that it may be shown ] -- or it is because many. Moreover, although the alloy content of No.9 was convention within the limits of this invention, since Zr was added independently, it did not result in the full dissolution but the overall diameter and consistency of inclusion separated from the convention range of this invention. Consequently, the number of repeats to fracture cannot reach a target, but the fatigue property is inferior. No.10 Although \*\* and inclusion are convention within the limits and the fatigue property is also excellent, since Fe and Ti component have separated from the convention range, conductivity has separated from the target (thermal conductivity is inferior).

[Example 2] In order to evaluate the effectiveness of casting size, they are the thickness of 300mm, and 400kg about the alloy of No.1 of Table 1. It cast to the ingot. Casting manufacture conditions, and subsequent processings - heat treatment conditions were made into an example 1 and these conditions (No.11: example of a comparison).

[0020] The property of the example of this invention of No.11 and No.1 acquired on this manufacture condition is compared, and it is shown in Table 4. Compared with the example of this invention, the amount of Zr system inclusion in which the cluster was formed increased the example of a comparison, and, as a result, the fatigue property fell remarkably.

[0021]

[Table 4]

	最大介在物サイズ ( $\mu\text{m}$ )	15~50 $\mu\text{m}$ 介在物密度 (個/ $\text{mm}^2$ )	機械的性質(300°C)			導伝率 (% IACS)	破断までの 繰返し回数 (10 <sup>5</sup> 回)	備考
			$\sigma_{0.2}$ ( $\text{kgf}/\text{mm}^2$ )	TS ( $\text{kgf}/\text{mm}^2$ )	EI (%)			
№1	14	0	38.5	40.0	10.5	85	5.1	本発明例
№11	97	5	36.7	37.8	10.0	86	1.9	比較例

The result shown in Table 3 and Table 4 shows that the good property of the balance which the examples of this invention are not only high temperature strength and high temperature transmissibility, but was excellent in the fatigue-proof property compared with the example of a comparison is shown.

[Example 3] In manufacturing the cooling roller for casting of the outer diameter of 900mm, the bore of 600mm, and 1000mm of drum length, 5.5t of alloys of table 1No.1 was cast, and hot forging, solution treatment, and cold forging were performed. The manufacture conditions in that case were made into an example 1 and these conditions (No.12: example of a comparison). On the other hand, similarly 2t of alloys of table 1No.1 was cast to the cooling roller for two-layer structure surfaces with an outer diameter [ of 900mm ], and a bore of 800mm, and hot forging, solution treatment, and cold forging were performed to it. The manufacture conditions in that case were also made into an example 1 and these conditions (No.13: example of this invention).

[0022] In addition, after casting and carrying out hot forging of the alloy of table 1No.1 the same also as a roll



for inner layers of the example of this invention and carrying out machining of the front face, it burned with the cooling roller for surfaces, and inserted in, and it combined by law. Example of a comparison acquired on this manufacture condition (No.12) Example of this invention (No.13) A surface property is compared and it is shown in Table 5. Compared with the example of this invention, the amount of Zr system inclusion in which the cluster was formed increased the example of a comparison, and, as a result, the fatigue property fell remarkably.

[0023]

[Table 5]

	最大介在物サイズ ( $\mu\text{m}$ )	15~50 $\mu\text{m}$ 介在物密度 (個/ $\text{mm}^2$ )	機械的性質(300°C)			導伝率 (% IACS)	破断までの繰り返し数 ( $10^5$ 回)	備考
			$\sigma^{0.2}$ ( $\text{kgf}/\text{mm}^2$ )	TS ( $\text{kgf}/\text{mm}^2$ )	El (%)			
No.12	215	13	35.8	38.1	9.8	82	0.9	比較例
No.13	14	0	38.5	40.0	10.5	85	5.1	本発明例